

\* A-category for all claims

## PATENT ABSTRACTS OF JAPAN

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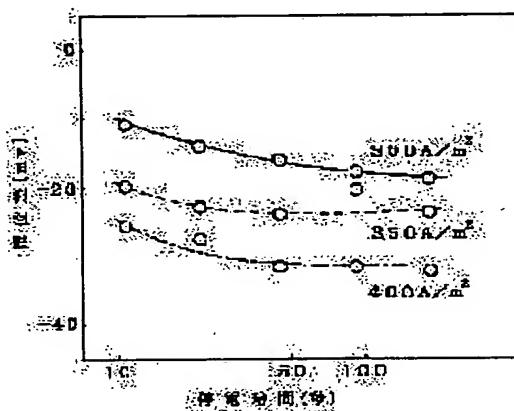
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TSUCHIDA NAORYUKI**(54) LONG PERIOD PULSE ELECTROLYTIC OPERATION IN ELECTROLYTIC COPPER REFINING**

(57)Abstract:

PROBLEM TO BE SOLVED: To reduce the percent defective of product by improving energizing system in a pulse electrolytic copper refining.

SOLUTION: The energizing system for periodically interrupting current for a fixed time is applied in a usual electricity conductive cycle in the electrolytic copper refining with high current density and when the energizing time in the positive direction is T, the current interruption time is T', T+T' is defined as 1 cycle and the cycle efficiency  $E_c(\%)$  is  $E_c=100 \times (T/(T+T'))$ , the cycle efficiency is kept  $\geq 5\%$  by holding the current interruption time preferably for  $\geq 30$ sec and controlling the cycle per 1hr to  $\leq 4$  times.

## LEGAL STATUS

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#### DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the graph which shows the relation between the potential difference until potential reaches a steady state after the right current energization start of cathode, and power failure time.

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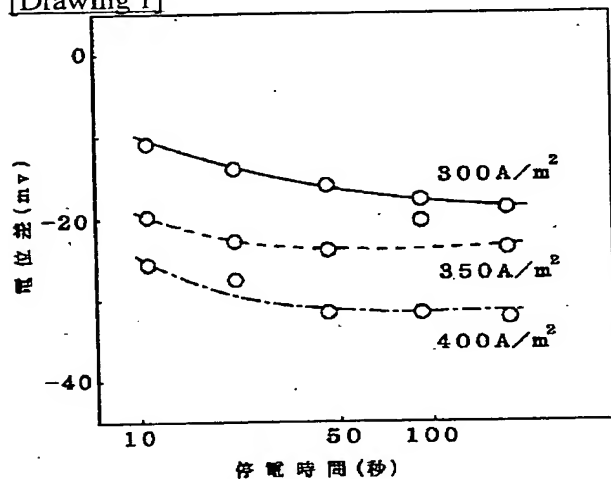
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DRAWINGS

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[Drawing 1]



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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Especially this invention relates to the operation method of copper electrorefining about copper electrolysis.

[0002]

[Description of the Prior Art] In copper electrorefining, although crude copper is used as an anode plate and a pure-copper board is usually used as cathode using the electrolytic solution containing the copper of 40 - 47 g/l, on a scale of the same cell, productivity goes up, so that current density is high. However, in the high current density (more than 300 A/m<sup>2</sup>) operation adopted for the improvement in productivity, there is a technical issue of generating of the passivation by the side of increase of the grain by the side of cathode and the percent defective of a phyma or the product negative plate accompanying generating of needlelike electrodeposition, a short increase, and an anode plate. On the other hand, for a passivation phenomenon, although influence is received in the impurity in an anode plate, the copper concentration in the electrolytic solution, surface lubricating agent concentration, etc., the influence by current density is large, and by the energization method of one usual direction, current density is 300 A/m<sup>2</sup>. It comes to regard as becoming above mostly. As a method of solving these problems, to consider as the pulse method with which only a short time stops current, or the periodic reversal current electrolysis (PRC) method with which only a short time reverses the sense of current is periodically confirmed in the energization method. However, generating of a grain, a phyma, and needlelike electrodeposition becomes remarkable with elevation of energization density, and is 300 A/m<sup>2</sup>. In the above current density, even if it applies the usual pulse electrolysis, aggravation of a surface electrocrystallization state is not avoided.

[0003] Moreover, to passivation prevention, the purpose can be attained about the power failure time of pulse electrolysis, and a cycle, without the conventional pulse electrolysis also worsening cycle efficiency. However, in order to maintain the surface state of cathode good, the conventional pulse electrolysis is inadequate. T and power failure time are defined as T', and cycle efficiency (%) defines  $T+T'$  for the resistance welding time of the right direction in pulse electrolysis as 1 cycle, and means  $EC = 100 \times (T/(T+T'))$  here. Furthermore, it is  $T' = 0.1 - 9$  seconds, and 1 cycle is a short short period method, in pulse (several 10 seconds - about 300 seconds) electrolysis of a short period method, since the conventional pulse electrolysis will perform a prolonged power failure, cycle efficiency falls and problems, like there is a problem economically produce it. Moreover, about short prevention, surface lubricating agents, such as glia and thiourea, were added to the electrolytic solution, and concentration of the current to the particular part of cathode is prevented. However, when these surface lubricating agents are used, the component is electrodeposited in cathode with copper, and there is a fault of reducing the purity of electrolytic copper. Moreover, it is known that use of a superfluous surface lubricating agent also makes short-circuit often increase. If the amount of a surface lubricating agent is managed appropriately, the surface state of cathode becomes good and short-circuit can be prevented. However, generally analysis of a surface lubricating agent is difficult, and cannot judge an effective dose easily correctly as a result. for this reason -- while observing the front face of cathode -- the addition of a surface lubricating agent -- not adjusting -- it has not necessarily come [ do not obtain, but there is

a limitation on use and ] to demonstrate the effect fully

[0004]

[Problem(s) to be Solved by the Invention] Therefore, this invention aims at reducing a product percent defective by improvement of an energization method in copper pulse electrorefining.

[0005]

[Means for Solving the Problem] this invention is 300 A/m<sup>2</sup>. In electrorefining of the copper in the above high current density, periodically, only fixed time adopts the pulse energization method which stops current, a pulse power failure is carried out 1 to 4 times in 1 hour, and 1 time of pulse power failure time is performed 30 seconds or more. Specifically, are made T and power failure time into T', and T+T' is made into 1 cycle for the resistance welding time of the right direction. By holding the stop time of current 30 seconds or more, and making the cycle per hour into 4 or less times, when cycle efficiency EC (%) in pulse electrolysis is defined as  $EC=100 \times (T/(T+T'))$  Cycle efficiency considers as 95% or more, and productivity is increased, without worsening the quality of a product negative plate.

[0006]

[Embodiments of the Invention] In this invention, only fixed time maintains the surface state of cathode good by the operation method in electrorefining of the copper in high current density in the energization method which stops current, and the so-called pulse electrolytic decomposition process periodically. It is the high current density 2, for example, 300 A/m, to drawing 1. In the above electrorefining, when changing power failure time, change of potential until potential reaches a steady state from a right current energization start, i.e., the relation between the potential difference and power failure time, is shown. Drawing 1 shows being completed as constant value by the potential difference in about 30 - 40 seconds power failure time. That is, if there is a power failure for 30 seconds or more, the surface state of cathode will be considered to be in the same state as the time of an energization start. In other words, surface lubricating agents, such as thiourea usually used by copper electrorefining, glue, and a chloride ion, are considered that the state where the cathode surface was adsorbed like the time of an energization start reappears by this power failure for 30 seconds or more. On the other hand, if power failure time exceeds 100 seconds, since it will be in a steady state, productive efficiency will only be lowered. Generally, a surface lubricating agent usually sticks to a surface granular portion, and it is interpreted as suppressing grain growth by reducing the electrodeposition rate of the portion. On the other hand, if current density rises, by concentration of the current to the grain section, and promotion of disassembly of the surface lubricating agent which stuck to the grain section, when the speed of supply on the front face of an electrode of the surface lubricating agent to the electrodeposition rate of the copper on an electrode falls relatively, the adsorbate concentration on the front face of an electrode will fall, and it will be thought that the granulation of cathode-surface electrocrystallization is caused as a result.

[0007] According to this invention, it is 300 A/m<sup>2</sup>. Also in the above operation of high current density, the power failure of comparatively long time is made to perform re-adsorption of a surface lubricating agent, and good electrocrystallization is obtained by supplying again the surface lubricating agent which the electrode front face runs short of. On the other hand, in the usual pulse electrolysis, the thing with a short cycle is because it has been pointed out that growth of the diffusion layer on the front face of an electrode increases with protraction of the resistance welding time. However, in industrial electrolysis like copper electrorefining, a big circulating flow exists in an electrode front face, and growth of the diffusion layer usually considered is sharply suppressed by the upflow by the circulating flow of a cathode surface, and the downflow by the free convection on the front face of an anode plate. Therefore, it is thought that the passivation by increase of the diffusion layer of an anode plate can prevent no less than one - two pulse power failures per hour. By constituting the cycle of a pulse power failure, specifically, by carrying out a pulse power failure about 1 to 4 times in 1 hour, and securing the power failure time in that case 30 seconds or more preferably, the passivation of an anode plate can be prevented also in operation of high current density, and the good smooth product negative plate of an electrocrystallization state is obtained by this invention based on the above theory. Furthermore,

in this invention, if it is the power failure of 1 - 4 times / hr, 95% or more is secured and, also economically, cycle efficiency can also attain improvement in advantageous productivity.

[0008]

[Example]

[Example 1] The point of the product negative plate at the time of changing the number of times of a cycle per hour evaluating [ appearance ] was investigated. The result is shown in Table 1. In addition, the energization conditions are as follows. Moreover, it is a totaling point at the time of performing 5 stage evaluations, having used [ the point evaluating / appearance / divided each both sides of a product negative plate into nine, and ] the best thing as five points by viewing, respectively having used the worst thing as one point (90-point full marks).

(Energization conditions)

Current density: 328 (A/m<sup>2</sup>)

Copper concentration: 52 (g/l)

Sulfuric-acid concentration: 188 (g/l)

Glue concentration: 1.4 (mg/l)

Chloride-ion concentration: 33 (mg/l)

Thiourea concentration: 1.1 (mg/l)

Solution temperature: 62 (degree C)

Anode plate: 1015x1015x36 (mm)

Cathode: 1050x1070x0.7 (mm)

Cathode number of sheets: 23 (sheet)

Cell: 3000x1250x1360 (mm)

[0009]

[Table 1]

Cycle composition Energization A power failure Cycle efficiency The number of times of a cycle  
Point evaluating [ appearance ] 59 (min) 1 (min) 98 (%) 1 (a time/hr) 69.5 59.5 (min) 0.5 (min) 98  
(%) 1 (a time/hr) 69.5 201 (s) 15 (s) 93 (%) 17 (a time/hr) 59.5 [0010] Table 1 shows that the  
point evaluating [ appearance ] is higher than that as which the direction adopted the so-called  
short periodical-pulse method power failure time was short, by the 17 number of times of a cycle /  
hr although the so-called long periodical-pulse method for having taken the power failure time for  
30 seconds or more by the one number of times of a cycle / hr was adopted. also in advance, this  
was described -- as -- a prolonged power failure -- a front face -- smooth re-adsorption is  
performed and it is thought that it originates in the surface smooth \*\*\*\*\* front face having been  
supplied enough Since the number of the management acceptance standards of the point  
evaluating [ appearance ] is usually 63, they can attain a management acceptance standard by  
adopting a long periodical-pulse method. Moreover, in the case of a long periodical-pulse method,  
95% or more is secured and, also economically, cycle efficiency is considered to be a satisfactory  
thing. On the other hand, as for the passivation of an anode plate, in any case, it was prevented  
completely.

[0011] [Example 2] energization conditions were changed to the example 1, and the point of the  
product negative plate at the time of changing the number of times of a cycle per hour with 1, 2,  
and 4 times evaluating [ appearance ] was investigated. The result is shown in Table 2. The  
energization conditions are as follows.

(Energization conditions)

Current density: 319-324 (A/m<sup>2</sup>)

Copper concentration: 47-53 (g/l)

Sulfuric-acid concentration: 187-191 (g/l)

Glue concentration: 1.4 (mg/l)

Chloride-ion concentration: 50 (mg/l)

Thiourea concentration: 2.2 (mg/l)

Solution temperature: 63.1-63.6 (degree C) Anode plate: 1015x1015x36 (mm)

Cathode: 1050x1070x0.7 (mm)

Cathode number of sheets: 25-27 (sheet)

Cell: 3000x1250x1360 (mm)

[0012]

[Table 2]

Cycle composition Energization A power failure Cycle efficiency The number of times of a cycle  
 Point evaluating [ appearance ] 59 (min) 1 (min) 98 (%) 1 (a time/hr) 71.5 29.4 (s) 34 (s) 98 (%) 2  
 (a time/hr) 71.5 14.7 (min) 16 (s) 98 (%) 4 (a time/hr) 69.5 [0013] In any case, Table 2 shows  
 having satisfied the management acceptance standard of the point evaluating [ appearance ] by the  
 long periodical-pulse method for having changed the number of times of a cycle to 1 - 4 times /  
 hr. However, in the four number of times of a cycle whose power failure time is 30 or less  
 seconds / thing of hr, it turns out that the fall of some point evaluating [ appearance ] is seen.  
 Since this has short power failure time, it is considered to originate in a surface lubricating agent  
 fully not having been supplied to an electrode front face between power failures. The four number  
 of times of a cycle / thing of hr is considered that power failure time will be secured about 45  
 seconds, and improvement in the point evaluating [ appearance ] can expect it further when cycle  
 efficiency is made into 95%, for example. Also about the example 2, the passivation of an anode  
 plate was completely prevented by each.

[0014]

[Effect of the Invention] According to this invention, in electrorefining of the copper in high  
 current density, only fixed time adopts periodically the energization method which stops current.  
 Are defined T and power failure time as T', and T+T' is defined for the resistance welding time of  
 the right direction as 1 cycle. When cycle efficiency EC (%) in pulse electrolysis is made into  
 $EC=100 \times (T/(T+T'))$ , hold the stop time of current 30 seconds or more preferably, and the cycle  
 per hour is made into 4 or less times. By maintaining cycle efficiency to 95% or more, it becomes  
 possible to increase productivity, without worsening the quality of a product negative plate.

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CLAIMS

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[Claim(s)]

[Claim 1] Current density is 300 A/m<sup>2</sup>. The long periodical-pulse electrolysis operation method characterized by carrying out a pulse power failure 1 to 4 times in 1 hour, and performing 1 time of pulse power failure time 30 seconds or more in the above copper electrorefining.

[Claim 2] Current density is 300 A/m<sup>2</sup>. In the above copper electrorefining, only fixed time adopts periodically the energization cycle method which stops current. Are defined T and power failure time as T', and T+T' is defined for the resistance welding time of the right direction as 1 cycle. The long periodical-pulse electrolysis operation method which makes the cycle per hour 4 or less times, maintaining cycle efficiency to 95% or more when cycle efficiency EC (%) in pulse electrolysis is made into  $EC=100 \times (T/(T+T'))$ , and is characterized by holding the stop time of the current for 30 seconds or more.

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[Translation done.]